

ac susceptibility and electron spin resonance studies of spin dynamics in $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$: A geometrically frustrated lattice

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Abstract

We report ac susceptibility and high-frequency electron spin resonance (ESR) measurements on the geometrically frustrated compound $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ with the Néel temperature $T_N = 27$ K. An unusually large frequency-dependence of ac susceptibility in the temperature range of 20 - 100 K reveals a spin-glass-like behavior, signalling the presence of frustration related slow magnetic fluctuations. ESR experiments show a multi-step magnetic and spin chirality ordering process. For temperatures above 30 K, the weak temperature dependence of the ESR linewidth $\Delta H_{pp} \propto T^{-p}$ with $p = 0.8$ evidences the development of short-range correlated spin clusters. The critical broadening with $p = 1.8$, persisting down to 14 K, indicates the coexistence of the short-range ordered spin clusters within a helically ordered state. Below 9.5 K, the anomalously large decrease of the linewidth reveals the stabilization of a long-range ordered state with one chirality.

Geometrically frustrated magnets are currently attracting intensive research interest in the context of condensed-matter physics.¹ Combined effects of quantum fluctuations and highly degenerate states lead to exotic ground states, a vortex-induced topological order, a long-range order in a higher-order degree of freedom such as scalar or vector chiral orders, quantum criticality as well as exotic low-lying excitations.^{2–10}

The simplest example of the frustrated antiferromagnets is found in the two-dimensional (2D) triangular lattice.¹¹ For the nearest-neighbor antiferromagnetic Heisenberg triangular system, the ground state is given by a 120° antiferromagnetic order.^{12–14} This invokes the notion of a vector spin chirality, which provides a conceptual framework for understanding phase transitions on the triangular lattices.

Among the triangular lattices the iron-based langasite $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ (BNFSO) is the focus of research interest due to its novel magnetic and multiferroic properties.^{15,16,19–23} BNFSO has a non-centrosymmetric trigonal structure belonging to the $P321$ space group. The Fe^{3+} ions ($S=5/2$) form isolated triangular lattices on a hexagonal lattice, which are arranged to form 2D triangular lattices in the ab plane. The neighboring planes are separated by layers containing Ba and Nb cations. A magnetic ordering occurs below the Néel temperature $T_N = 27 \text{ K}$ despite a large Curie-Weiss temperature of $\Theta_W = -173 \text{ K}$, signifying substantial frustration. The intratriangle interaction of $J_1 \approx 9.9 \text{ K}$ is mediated by superexchange via oxygen anions forming the tetrahedral coordination. The intertriangle interaction of $J_2 \approx 2.8 \text{ K}$ in the ab plane is mediated by two oxygens (super-superexchange). Besides, a set of interplane exchange pathways are needed to stabilize the helical spin structure along the c axis with the period $1/\tau \approx 7$. Even without applying an external field chiral dynamics is observed from spin-wave excitations of the helically modulated 120° magnetic order.²² This means that BNFSO is a rare example possessing both a triangular chirality and a helical chirality in a single lattice.

Neutron scattering experiments reveal a multi-step magnetic ordering process towards a single chirality phase.¹⁶ Vortices ordering is considered to play a crucial role in relation to the multiferroic properties. Frustrated magnets show a many-sided face, depending on the time- and spacescales of employed spectroscopic methods. Thus, it is important to investigate a spin and chirality ordering process using a different time window from neutron scattering. ac susceptibility and electron spin resonance (ESR) are a complimentary experimental choice because the former can probe a slow spin dynamics while the latter is sensitive to fast

short-range spin correlations.

In this brief report, we present evidence for the spin-glass-like slow spin dynamics by ac susceptibility, and for the persistence of short-range correlated spin chirality states well down to T_N by ESR. The simultaneous observation of the *slow* and the *fast* spin dynamics might be the characteristic feature of frustrated magnets with a large spin value and spin chirality.

Single crystals of BNFSO were grown using the travelling-solvent floating-zone technique as described elsewhere.¹⁵ The crystals were characterized using X-ray diffraction, magnetic susceptibility, specific heat, thermal conductivity, neutron scattering, dielectric and polarization measurements.^{15,16} ac susceptibility measurements were performed as a function of temperature using a SQUID magnetometer (Quantum Design MPMS) in a frequency range $\nu = 1 - 1000$ Hz in an ac field of 3 Oe and zero dc magnetic field. The high frequency-ESR spectra were obtained on the ESR spectrometers at the National High Magnetic Field Laboratory. The temperature dependence was measured using a homodyne/transmission spectrometer at $\nu = 100$ GHz.^{17,18}

Figure 1 shows the temperature dependence of the ac susceptibility taken in zero dc magnetic field. With decreasing temperature the real part of the ac susceptibility, $\chi'(T)$, for $\nu = 1$ Hz exhibits a round maximum at 39 K and then a kink around $T_N \sim 27$ K. With increasing frequency, the maximum shifts to higher temperature and decreases in amplitude. The kink at T_N evolves into a sharp peak without changing the position. This feature is due to critical fluctuations accompanying a transition to the Néel ordered state.

The imaginary part of the ac susceptibility, $\chi''(T)$ also exhibits appreciable frequency dependence between 20 K and 100 K. The loss peak of $\chi''(T)$ is visible for $\nu = 1$ Hz at 32 K, which is 7 K lower than that in $\chi'(T)$. With increasing ν , the peak undergoes a shift to higher temperatures. and the peak width broadens. In contrast to $\chi'(T)$, there is no decrease in amplitude. Overall, these features are reminiscent of a spin-glass-like behavior or superparamagnetism. However, it should be discriminated from conventional spin glasses due to the following reasons.

First, the dc susceptibility does not show any round maximum in contrast to the ac susceptibility. Second, the magnitude of the frequency shift is much larger than what is expected for canonical spin glasses. We used the well-defined peak position of $\chi''(T)$ to estimate the shift of the ac susceptibility as a function of frequency (see the inset of Fig. 1).

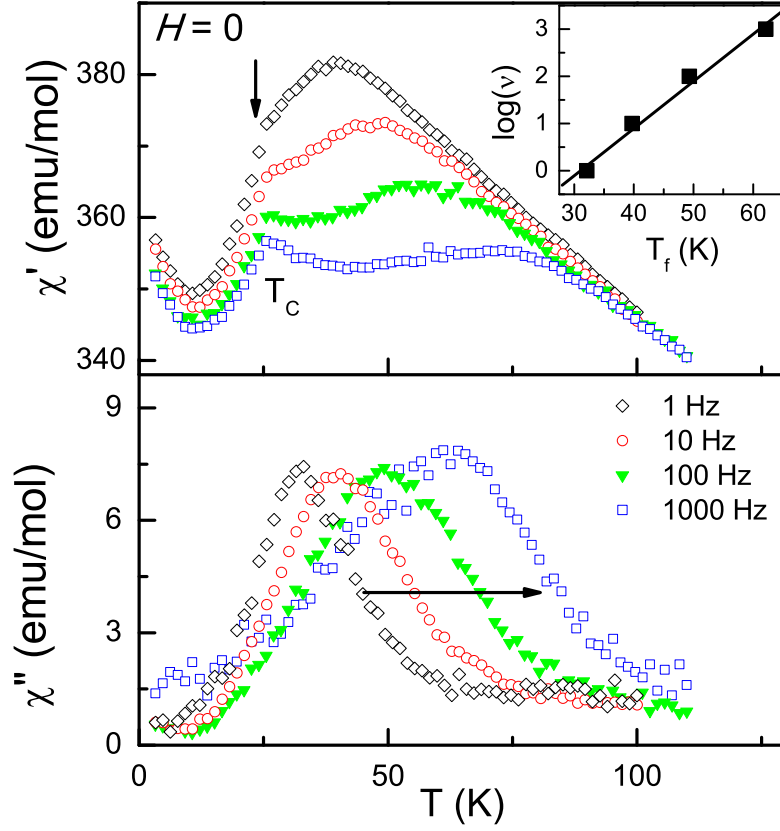


FIG. 1: Temperature dependence of the real and imaginary parts of the ac susceptibility at frequencies $\nu = 1, 10, 100$, and 1000 Hz without external dc field. With increasing frequency the ac susceptibility curve shifts to higher temperatures (see the arrow). Inset: Frequency shift of the peak position of the imaginary part of the ac susceptibility versus temperature.

The curve shifts by as much as 30 K on varying the frequency from 1 Hz to 1000 Hz. From the maximal shift ΔT_f we obtain the value of $\phi = \Delta T / T_f \Delta(\log \nu) \sim 0.16$. This value is much bigger than that of a spin glass, which is typically the order of 10^{-2} .²⁴ The large ϕ is compatible to some sort of superparamagnetism.

Similar features have been reported in pyrochlores and spin-chain compound $\text{Ca}_3\text{CoIrO}_6$ with magnetic frustration.^{25,26} This suggests that the strong frequency dependence of the ac susceptibility originates from a slow spin dynamics pertaining to geometrically frustrated magnets, akin to superparamagnetism.

In addition to the observed slow spin dynamics, the 2D triangular antiferromagnets are characterized by fast short-range magnetic correlations over a space scale of a spin trimer.

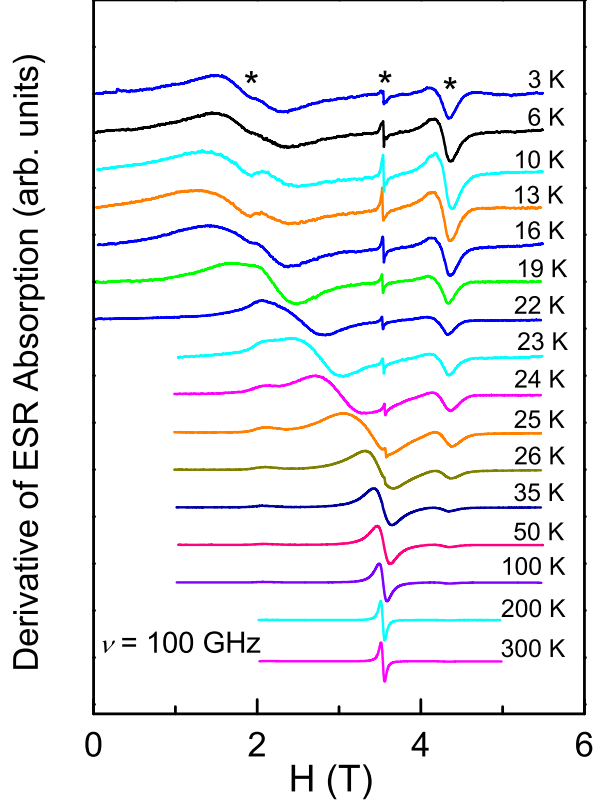


FIG. 2: Derivative of the ESR absorption of the BNFSO sample measured at $\nu = 100$ GHz as a function of temperature. The asterisks denote impurities or parasitic phases, since they exhibit no shift with temperature.

It is known that high-frequency ESR can provide direct information on the evolution of spin correlations. Figure 2 shows the temperature dependence of the ESR spectra measured at 100 GHz. At room temperature, a narrow single Lorentzian line is observed, originating from $\text{Fe}^{3+}(3d^5; S = 5/2)$ ions. The g-factor is close to the free spin value as expected from a half-filled ($3d^5$) shell. With decreasing temperature the spectrum undergoes a broadening and a shift to lower fields. In addition to the main signal, at low temperatures extra peaks show up. Their peak positions do not change with temperature and their intensities show a Curie-like behavior. Thus, they are ascribed to a few percentage of impurities or parasitic phases. Hereafter, we will focus on the main signal. To detail the evolution of the spectrum, the resonance field (H_{res}) and the ESR linewidth (ΔH_{pp}) are extracted by fitting the spectra to a derivative of Lorentzian profiles. The results are plotted as a function of temperature

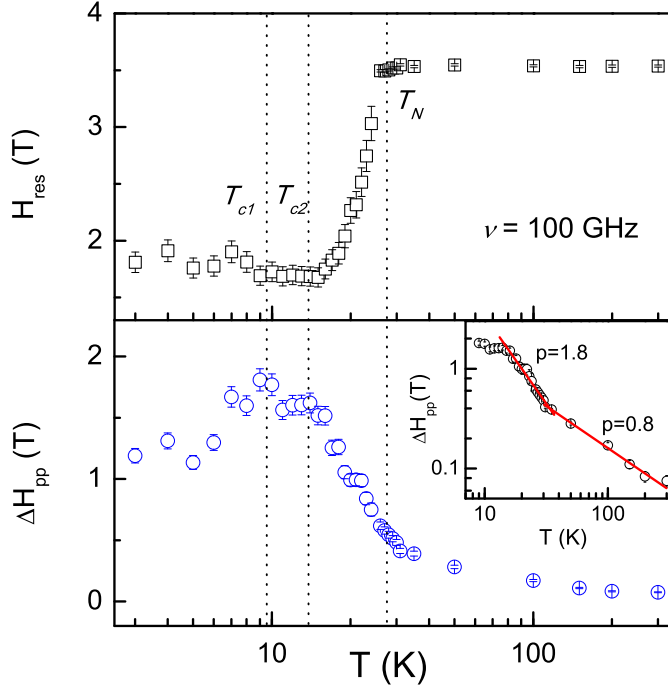


FIG. 3: Temperature dependences of the resonance field, H_{res} , (upper panel) and the ESR linewidth, ΔH_{pp} in a semilogarithmic plot (lower panel). Inset: A log-log plot of ΔH_{pp} versus temperature. The solid lines are a fit to a power law. See the text for details.

in Fig. 3.

We observe intriguing features in the temperature dependence. For temperatures above 30 K ($T > T_N$), ΔH_{pp} increases gradually with lowering temperature while H_{res} hardly varies with temperature. At temperatures between 30 K and $T_{C2} = 14$ K, the linewidth increases enormously and the resonance field shifts strongly toward lower fields. In the short temperature interval between $T_{C1} = 9.5$ K and T_{C2} both ΔH_{pp} and H_{res} show no apparent temperature dependence. Finally, for temperatures below T_{C1} , H_{res} does not change with temperature while ΔH_{pp} drops but it remains at a large value even at the lowest temperature.

To analyze quantitatively the temperature dependence of the linewidth, ΔH_{pp} is plotted in a log-log scale as shown in the inset of Fig. 3. We find the weak power law dependence, $\Delta H_{pp} \propto T^{-p}$ with $p = 0.8$ for $T > 30$ K and the strong temperature dependence with $p = 1.8$ between T_{C2} and T_N .

For conventional magnets, the linewidth is temperature independent in a high-

temperature paramagnetic regime and starts to broaden in the vicinity of magnetic ordering temperature. In contrast, frustrated magnets exhibit significant temperature dependence of the linewidth in a wide temperature range reaching up to a dozen times the ordering temperature. It is due to short-range spin correlations over a spin cluster unit. In our case, the neutron experiments demonstrated the persistence of correlated magnetic scattering with a vector chiral component up to 100 K²³ and the presence of diffuse scattering at an order of the Curie-Weiss temperature, Θ_W .¹⁶ Noticeably, the 2D triangular-lattice NiGa_2S_4 with a low spin value $S=1$ showed pronounced T-dependence of ΔH_{pp} with the critical exponent $p = 2.5$.²⁷ The observed smaller exponent for BNFSO suggests that the spin dynamics and critical fluctuations of the studied compound are in proximity to the classical limit due to a larger spin value $S = 5/2$. This might be responsible for the observation of the slow spin dynamics by ac susceptibility.

An unconventional feature is seen as temperature approaches T_N . The large shift of H_{res} to a lower field for $T < T_N$ implies the development of an internal magnetic field. This is what is expected for a magnetically ordered state. Instead of the expected line narrowing, however, the linewidth shows a critical broadening $\Delta H_{pp} \propto T^{-p}$ with $p = 1.8$, which starts at about 30 K, higher than T_N and persists down to 14 K. The onset temperature reminds us of the temperature scale of 40 K, at which the neutron measurements show a development of long-range correlations and the heat capacity and thermal-conductivity measurements show broad anomalies.^{15,16} In addition, the neutron scattering study revealed the presence of the diffusive scattering down to 20 K, which is close to T_{C2} . This feature is ascribed to the coexistence of short-range ordered spin clusters within the helically ordered state as has been reported for other frustrated magnets.²⁸ In our case, it might be due to spin clusters of opposite chirality generated by defects and impurities.

In a magnetically ordered state the ESR linewidth is determined by four magnon scattering processes and an occupation number of magnon excitations. Thus, with lowering temperature the linewidth decreases with a power law. BNFSO shows the drop of ΔH_{pp} at about $T_{C1} \approx 9.5$ K. This suggests that a true long-range ordered state with one chirality sets in at T_{C1} . However, the large linewidth at the lowest temperature of 3 K indicates that there are the significant fluctuations of the uniform spin chirality in the measured time scale of $\nu = 100$ GHz. Finally, we turn to the transit temperature interval between T_{C1} and T_{C2} . This rather flat feature in ΔH_{pp} seems to indicate the competition between the narrowing

and the broadening mechanism. Unlike the $S=1$ triangular compound NiGa_2S_4 , we find no hint for the bound state of a \mathbb{Z}_2 vortex.

In summary, we have presented a combined ac susceptibility and ESR study of $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$. We observe a spin-glass-like behavior of the ac susceptibility in a wide temperature range of 20 - 100 K, but with much larger Mydosh parameter, suggesting superparamagnet due to locally ordered clusters. The ESR measurements reveal the persistence of a short-range correlated state to a long-range ordered one. The concomitant occurrence of frustration related *slow* and *fast* spin dynamics might be a generic feature of frustrated magnets with a large spin value and a well-defined spin chirality. For more quantitative understanding, we need systematic studies of the spin dynamics in the $10^3 - 10^{11}\text{s}^{-1}$.

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